

⑫

EUROPEAN PATENT APPLICATION

⑰ Application number: 86308565.0

⑱ Int. Cl.4: **A 61 K 7/32**

⑳ Date of filing: 03.11.86

㉑ Priority: 04.11.85 US 794981

㉒ Date of publication of application:
20.05.87 Bulletin 87/21

㉓ Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

㉔ Applicant: **CALGON CORPORATION**
Route 60-Campbell's Run Road
Robinson Township Pennsylvania 15205 (US)

㉕ Inventor: **Klein, William L.**
454 Chestnut Street
Nutley New Jersey 07110 (US)

Sykes, Arthur R.
23 Brooktree Road
East Windsor New Jersey 08520 (US)

㉖ Representative: **Crompton, Keith John Allen et al**
D YOUNG & CO 10 Staple Inn
London WC1V 7RD (GB)

㉗ Antiperspirant formulations containing quaternary ammonium polymer.

㉘ Stable antiperspirant compositions comprise an antiperspirant and a polymer of dimethyldiallyl ammonium chloride, which serves to increase the residual amount of the antiperspirant on a surface such as the skin.

EP 0 222 580 A1

Description

ANTIPERSPIRANT FORMULATIONS CONTAINING QUATERNARY AMMONIUM POLYMER

This invention relates to antiperspirant compositions. Numerous literature references disclose detergent compositions for cosmetic and personal use, such as shampoos, antiperspirant formulations and anti-dandruff rinse conditioners that contain anionic and/or cationic polymers, an active agent, surfactants, emollients, and other additives and preservatives common in the industry, as discussed below.

U.S. Patent Specification US-A-3 761 417 is directed to detergent compositions containing particle-deposition-enhancing agents, more specifically, toilet detergent bars containing water-insoluble particles such as antimicrobial agents, organic surfactants and cationic polymers. Surfactants are an essential ingredient of the compositions. Dimethyldiallyl ammonium chloride (DMAAC) is specifically mentioned as a possible cationic polymer.

US. Patent Specification US-A-3 769 398 discloses non-anionic hair shampoo formulations containing an active ingredient (a detergent such as a betaine, sulfobetaine or amine oxide or a mixture thereof), a water-soluble polymer (polyethylenimine-ethylene oxide or propylene oxide) and propoxylated polyethylenimines.

U.S. Patent Specification US-A-4 329 335 describes an amphotericnonionic anti-dandruff shampoo containing 1-imidazolyl-1-(4-chlorophenoxy)-3,3-dimethylbutan-2-one and amphoteric surfactants polyoxyethylene hexitan mono or higher fatty acid ester, tertiary amine oxide, fatty acid mono- or di-ethanolamide and optionally a polymerized quarternized ammonium compound. DMAAC is specifically disclosed as a preferred polymerized quarternized ammonium compound.

European Patent Specification EP-A-0 074 819 discloses an anti-dandruff cream rinse conditioner of DMAAC-acrylamide, glucan or guar gum and hydroxyethylcellulose.

European Patent Specification EP-A-0 055 857 discloses the preparation of topically applied compositions comprising ultraviolet-light-absorbing materials and film-forming polymers and exhibiting enhanced protection from erythema-causing radiation.

It has now been found that stable and effective antiperspirant compositions can be prepared comprising at least one antiperspirant and one or more polymers of dimethyldiallyl ammonium chloride, and that the polymer increases the amount of antiperspirant on the surface to which it is applied, thereby enhancing its effect and making a lower dosage of the antiperspirant effective, thereby reducing possible future side effects.

The present invention provides an antiperspirant composition comprising at least one antiperspirant agent and a polymer of dimethyldiallyl ammonium chloride.

Also in accordance with the invention, body secretion is treated by topically applying such a composition to the skin.

The compositions of the present invention are thus capable of being topically administered. They may optionally contain cosmetically acceptable excipients such as buffers and/or preservatives. The polymer is present in an amount sufficient to enhance deposition and/or retention of the antiperspirant agent on the intended surface. The composition may be prepared by agitating the polymer, with or without de-ionized water, optionally adding an emulsifier with continued agitation, heating to a temperature ranging from ambient to 90°C (preferably 65° to 80°) until a uniform mixture is obtained, and continuing agitation while adding an antiperspirant agent, optionally followed by preservatives, thickening agents, buffers, dyes and/or fragrances, and ultimately adjusting the formulation by adding de-ionized water while maintaining the temperature. The polymer can be added at any stage of the procedure.

The amount of the antiperspirant agent varies over a wide range and depends on the specific agent involved. Usually, the antiperspirant effective amount would be considerably less than that previously believed necessary to obtain the desired results. Specifically, the amount of antiperspirant agent used in the formulations herein usually constitutes from 0.01% to 50% and preferably 5% to 20% of the total weight of the composition. If the only components are antiperspirant agents and polymers, the amount can be up to 99.09% by weight.

The amount of polymer used in the practice of the invention ranges from 0.01% to 12% polymer, preferably 1% to 3%, by weight of the composition, the remainder being the antiperspirant agent and optional conventional acceptable excipients.

Polymers of dimethyldiallyl ammonium chloride (DMAAC) include both homopolymers and copolymers of DMAAC. The copolymer should contain at least 10% by weight of DMAAC. A homopolymer is preferred. An example of a homopolymer of DMAAC is that sold under the registered trade mark Merquat 100, which is manufactured by Calgon Corporation and which has an intrinsic viscosity of 0.3 dl/g in 1.0 M NaCl. Although any copolymers (including terpolymers and polymers of more than three monomers) may be used, the preferred copolymers are DMAAC/acrylamide and DMAAC/acrylic acid.

Example of copolymers of dimethyldiallyl ammonium chloride (DMAAC) and acrylamide, are Merquat S and Merquat 550.

The preferred product is Merquat S. Merquat 550 and S copolymers have an intrinsic viscosity of 4.2 ± 0.2 in 1.0 M NaCl and contain, by weight, about 50 percent DMAAC and 50 percent acrylamide.

Although any ratio of DMAAC and comonomer will work, the preferred ratio is 10 to 75 percent, particularly 25 to 75 percent, by weight, DMAAC and, correspondingly, 25 to 90 percent, particularly 25 to 75 percent, by

weight, comonomer.

Polymers of DMDAAC used in the invention have a molecular weight ranging from 20,000 to 2,500,000, preferably from 200,000 to 300,000, and an intrinsic viscosity of 0.1 to 2.5, preferably from 0.7-0.9, in 1.0M NaCl.

Representative antiperspirant agents used in the practice of the invention are aluminium zirconium complexes such as those sold under the registered Trade Marks Rezal 36GP (aluminium zirconium tetrachlorohydrate-glycine) and Rezal 67 (aluminium zirconium pentachlorohydrate), aluminium chlorohydrate, aluminium chlorohydroxide, aluminium chlorohydrate, aluminium chlorohydrate P.G., aluminium sulphate and potassium alum.

Representative emollients, emulsifiers, humectants and moisturising agents that can be used in the compositions of the invention are C₁₂₋₁₅alcohol benzoates, SDA40 alcohol, stearyl alcohol, sorbitol, Volpo 3100, glycerin, glyceryl stearate, propylene glycol (PEG), lanolin, talc, vegetable oils, mineral oils, isopropyl myristate, aloe vera, cyclomethicone, jojoba oil, PEG 100 stearate, cetyl esters, PPG-15 stearyl ether and steareth 2 and 21.

Other cosmetically acceptable excipients that the formulation may contain are thickening agents, buffering agents and preservatives. Suitable water soluble preservatives are sodium bisulphite, sodium thiosulphate, ascorbates, benzalkonium chloride, glydant, 1,3-bis(hydroxymethyl)-5,5-dimethyl-2,4-imidazolidinedione, chlorobutanol, thimerosal, phenylmercuric borate, Dowicil 200, 1-(3-chloro-2-propenyl)-3,5,7-triaza-1-azonia-tricyclo[3.3.1.1]decane, parabens, Tektamer 38 (1,2-dibromo-2,4-dicyanobutane), benzyl alcohol and phenylethanol. Suitable thickening agents are those sold under the registered Trade Marks Cab-O-Sil M5, Carbomer 934, 940 and 941, sodium stearate, magnesium aluminium silicate and hydroxyethyl cellulose. These agents, may optionally be present in amounts of from 0.05 to 50% by weight, preferably 1 to 5%. Suitable watersoluble buffering agents include alkali or alkaline-earth metal carbonates, phosphates, bicarbonates, citrates, borates, acetates, acid anhydrides and succinates, such as sodium phosphate, citrate, borate, acetate, bicarbonate and carbonate. These agents may be present in amounts sufficient to maintain the optimum pH of the system in the range 2 to 9. As such the buffering agent can be as much as 20% on a weight to weight basis of the total composition.

Studies were conducted on the degree of retention of aluminium on the skin with and without a polymer.

TABLE I
RETENTION OF ALUMINUM ON SKIN

5	<u>Samples</u>	<u>Treatment</u>	<u>Results</u> <u>(PPM)</u>
10	A. Control	Skin sample treated with 150 µl of aluminum chlorohydrate P.G. anti- 15 perspirant solution followed by 15-second 20 tap water rinse	0.4*
25	B. Experiment	Skin sample treated with 150 µl of aluminum chlorohydrate P.G. anti- perspirant solution with 30 2% Merquat 100 followed by 15-second tap water rinse	0.8*

35
*same results for two (2) experiments

40 The above results clearly illustrate that formulation B which contains a polymer is twice as effective as
formulation A without a polymer in the retention of aluminium on the skin.

The following examples illustrate the preparation of various antiperspirant formulations of the invention. The
Examples do not limit the invention.

EXAMPLE 1Stick Antiperspirant Control Formulation*

NO.	PHASE	INGREDIENT	% BY WEIGHT
1	A	cyclomethicone	46.20
2	A	glyceryl stearate and PEG 100 stearate	1.00
3	B	stearyl Alcohol	20.00
4	B	Volpo 3100	10.00
5	B	Rezal 36GP	20.00
6	C	talc	1.00
7	D	triclosan	0.20
8	D	Cab-O-Sil M5	1.00
9	E	fragrance	<u>0.60</u>
		q.s.	100.00

*Without polymer

With rapid agitation, phase A ingredients were thoroughly mixed and heated to 65°C while phase B ingredients were individually added and stirred until dissolved. The solution was stirred for approximately 5 minutes while adding phase C. When dissolved, the resulting phases D were added individually and stirred for 15 minutes and phase E was added, agitated until dissolved and q.s. to 100%. The resulting mixture was then poured into the suitable containers for personal care application. The temperature was maintained at 65°C while making the additions.

EXAMPLE 2

5

Stick Antiperspirant

	NO.	PHASE	INGREDIENT	% BY WEIGHT
10				
	1	A	cyclomethicone	44.20
15	2	A	glyceryl stearate and PEG 100 stearate	1.00
	3	B	stearyl Alcohol	20.00
20	4	B	Volpo 3100	10.00
	5	B	Rezal 36GP	20.00
	6	C	talc	1.00
25	7	D	triclosan	0.20
	8	D	Cab-O-Sil M5	1.00
	9	E	perfume	0.60
30	10	E	Merquat 100	<u>2.00</u>
				100.00

35 The procedure and reaction conditions of Example 1 were followed except that "Merquat 100" was added with phase E ingredients to obtain the corresponding product.

40

45

50

55

60

65

EXAMPLE 3Stick Antiperspirant

NO.	PHASE	INGREDIENT	% BY WEIGHT	
1	A	cyclomethicone	43.20	5
2	A	glyceryl stearate and PEG 100 stearate	1.00	10
3	B	stearyl Alcohol	20.00	15
4	B	Volpo 3100	10.00	20
5	B	Rezal 36GP	20.00	
6	C	talc	1.00	
7	D	triclosan	0.20	25
8	D	Cab-O-Sil M5	1.00	
9	E	fragrance	0.60	
10	E	Merquat S	<u>3.00</u>	30
			100.00	

With rapid agitation, phase A ingredients were thoroughly mixed and heated to 65°C. Phase B ingredients were individually added to phase A and stirred for 5 minutes. Phase C ingredient was added and stirred for 5 minutes. Phase D ingredients were individually added and stirred for 15 minutes. With continued agitation, phase E ingredients were added individually and stirred until dissolved. The resulting mixture was then stirred an additional 15 minutes. This mixture was then poured into the suitable containers for personal care application. The temperature was maintained at 65°C while making the additions.

Following the above reaction conditions and procedure, aluminium chlorohydrate, aluminium sulphate, potassium alum, aluminium chlorohydrate, or aluminium chlorohydrate P.G. may be substituted for aluminium zirconium tetrachlorohydrate complex, to obtain the corresponding stick antiperspirant formulation.

EXAMPLE 4Roll-on Antiperspirant

5	NO.	PHASE	INGREDIENT	% BY WEIGHT
10				
	1	A	cyclomethicone	44.20
15	2	A	glyceryl stearate and PEG 100 stearate	1.00
	3	B	Merquat 100	2.00
20	4	B	stearyl alcohol	20.00
	5	B	silica	1.00
	6	B	Volpo 3100	10.00
25	7	C	aluminum zirconium tetra- chlorohydrate complex	20.00
	8	C	talc	1.00
30	9	D	preservative & fragrance	<u>qs</u>
			q.s.	100.00

35

In separate vessels, the ingredients of phases A and B were heated to 65°C. With agitation, phase B was added to phase A, cooled to 65°C and phase C ingredients were added. Agitation was continued and the reaction mixture was cooled and phase D ingredient added.

40

45

50

55

60

65

EXAMPLE 5Antiperspirant Cream

NO.	PHASE	INGREDIENT	% BY WEIGHT
1	A	cetyl alcohol	4.00
2	A	glyceryl stearate and PEG 100 stearate	10.00
3	B	Merquat 100	2.00
4	B	sorbitol	3.00
5	B	deionized water	41.00
6	C	aluminum zirconium tetra- chlorohydrate complex	40.00
7	D	preservative & fragrance	
		q.s.	100.00

In separate vessels, the ingredients of phases A and B were heated to 75°C and 78°C, respectively. With agitation, phase B was added to phase A, cooled to 40°C and phase C ingredients were added. Agitation was continued and the reaction mixture was cooled and poured into suitable containers for personal care application.

EXAMPLE 6Liquid Antiperspirant

NO.	PHASE	INGREDIENT	% BY WEIGHT
1	A	SDA 40 alcohol	25.00
2	A	glycerine	4.00
3	B	aluminium chlorohydrate	30.00
4	C	deionized water	35.80
5	D	Merquat 100	2.00
6	E	preservative & fragrance	
		q.s.	100.00

In the same vessels, the ingredients of phases A and B were added and mixed until a clear solution was obtained. With agitation, phases C and D were premixed and added to the reaction mixture. Agitation was

continued until the reaction mixture was uniform, phase D ingredient added and poured into suitable containers for personal care application.

5

EXAMPLE 7

10

Antiperspirant Lotion

15

NO.	PHASE	INGREDIENT	% BY WEIGHT
1	A	PPG-15 stearyl ether	4.00
2	A	steareth 21	.60
3	A	steareth 2	2.60
4	B	deionized water	50.80
5	B	Merquat 100	2.00
6	C	aluminum zirconium tetra- chlorohydrate-glycine	40.00
7	D	preservative & fragrance	
		q.s.	100.00

In separate vessels, the ingredients of phases A and B were heated to 75°C and 78°C, respectively. With agitation, phase B was added to phase A, cooled to 40°C and phase C ingredient was added. Agitation was continued, phase D ingredient was added and the reaction mixture was cooled and poured into suitable containers for personal care application.

40

45

50

55

60

65

EXAMPLE 8**Stick Antiperspirant**

NO.	PHASE	INGREDIENT	% BY WEIGHT	
<hr/>				
1	A	isopropyl myristate	2.00	
2	A	propylene glycol	20.30	15
3	B	propylene glycol	2.00	
4	B	titanium dioxide	0.20	
5	C	isostearyl alcohol	11.30	20
6	D	stearamide MEA	26.00	
7	E	SDA 40 alcohol	14.50	25
8	E	aluminium chlorohydrate P.G.	20.00	
9	F	triclosan	0.20	30
10	G	Merquat S	<u>3.00</u>	
11	H	preservatives and fragrances q.s.	100.00	35

With rapid agitation, phase A ingredients were thoroughly mixed and heated to 65°C. Phase B ingredients were thoroughly mixed added to phase A with continued agitation. Phase C ingredient was added stirred for 5 minutes and the reaction mixture heated to 80°C. Phase D ingredient was added and stirred to obtain uniformity. With continued agitation, the reaction was cooled to 76°C and phase E ingredients were added individually and stirred until dissolved. The resulting mixture was then briefly stirred and phases F, G and H were successively added. This mixture was then poured into the suitable containers for personal care application.

Claims

1. An antiperspirant composition comprising at least one antiperspirant agent and a polymer of dimethyldiallyl ammonium chloride. 50
2. A composition as claimed in claim 1, further comprising water.
3. A composition as claimed in claim 2, in which the antiperspirant agent is aluminium zirconium complex, aluminium sulphate, potassium alum, aluminium chlorohydrate, aluminium chlorohydroxide, aluminium chlorohydrate or aluminium chlorohydrate P.G. 55
4. A composition as claimed in claim 4, in which the antiperspirant agent is aluminium zirconium complex, aluminium chlorohydrate P.G. or a combination thereof.
5. A composition as claimed in claim 4, in which the antiperspirant agent is aluminium zirconium tetrachlorohydroxy-glycine and/or aluminium zirconium pentachlorohydrate. 60
6. A composition as claimed in any one of claims 2 to 5, in which the polymer is a homopolymer of dimethyldiallyl ammonium chloride.
7. A composition as claimed in any one of claims 2 to 5, in which the polymer is dimethyldiallyl ammonium chloride/acrylamide or dimethyldiallyl ammonium chloride/acrylic acid.
8. A composition as claimed in claim 7, in which the copolymer contains 10 to 75 percent by weight 65

dimethyldiallyl ammonium chloride and 25 to 90 percent by weight acrylamide.

9. A composition as claimed in any one of claims 2 to 8, further comprising cosmetically acceptable excipients.

10. A composition as claimed in claim 1 for use in treating body secretion by being topically administered to the skin.

5

10

15

20

25

30

35

40

45

50

55

60

65



EP 86 30 8565

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	EP-A-0 018 137 (McLAUGHLIN GORMLEY KING CO.) * Example 22 *	1-3, 6, 9, 10	A 61 K 7/32
Y	GB-A-2 004 743 (L'OREAL) * Whole document *	1-7, 9, 10	
Y	GB-A-2 113 706 (COLGATE-PALMOLIVE) * Whole document *	1-7, 9, 10	
Y	US-A-4 174 386 (SPITZER et al.) * Whole document *	1-7, 9, 10	
A	SOAP, PERFUMERY & COSMETICS, vol. 57, no. 7, July 1984, pages 351, 355, London, GB; P. ALEXANDER: "Merquat - its qualities and applications" * Page 351, middle column, line 11 *	1	<div>TECHNICAL FIELDS SEARCHED (Int. Cl. 4)</div> A 61 K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22-01-1987	Examiner FISCHER J.P.
<div>CATEGORY OF CITED DOCUMENTS</div> <div> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document </div>			



EUROPEAN PATENT APPLICATION

Application number : **91308792.0**

Int. Cl.⁵ : **A61K 7/32, A61K 7/48,
A61K 7/06**

Date of filing : **26.09.91**

Priority : **28.09.90 US 589362**

Date of publication of application :
01.04.92 Bulletin 92/14

Designated Contracting States :
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

Applicant : **CALGON CORPORATION**
Route 60-Campbell's Run Road
Robinson Township Pennsylvania 15205 (US)

Inventor : **Melby, Allan L.**
104 Heathercroft Drive
Zellenople, PA 16063 (US)
Inventor : **Boothe, Jerry E.**
221 Disney Drive
Coraopolis, PA 15108 (US)

Representative : **Barrett-Major, Julie Diane et al**
Merck & Co., Inc. European Patent
Department Terlings Park Eastwick Road
Harlow Essex CM20 2QR (GB)

Method for thickening metal-containing products using DMDAAC/acrylic acid-type polymers.

A method for thickening metal-containing aqueous solutions, particularly personal care products, such as aluminum-containing antiperspirants, is disclosed. The method comprises adding an effective amount for the purpose of at least one dimethyl diallyl ammonium chloride/acrylic acid-type polymer.

EP 0 478 327 A1

BACKGROUND OF THE INVENTION

The instant invention relates to the thickening of metal-containing aqueous solutions, such as personal care product formulations, particularly liquid antiperspirant formulations which contain aluminum, by the addition of an effective amount of at least one dimethyl diallyl ammonium chloride (DMAAC)/acrylic acid-type polymer. These polymers increase the thickness or viscosity of aqueous metal-containing solutions such as personal care product formulations and the like, and generally do not impart color to water-white formulations being thickened.

Numerous references disclose cosmetic and personal care compositions, such as shampoos, antiperspirant formulations, anti-dandruff rinse conditioners, etc., which contain anionic and/or cationic polymers, an active agent, surfactants, emollients and other additives and preservatives commonly employed in the industry. Pertinent references which relate to DMAAC polymers or which disclose cosmetic and personal care formulations containing DMAAC polymers include:

1. U.S. Pat. No. 3,761,417, which is directed to detergent compositions containing particle deposition enhancing agents. More particularly, this patent discloses detergent and personal use detergent bars which contain water-soluble particles such as antimicrobial agents, surfactants and cationic polymers. Possible cationic polymers include dimethyl diallyl ammonium chloride polymers (DMAAC).
2. U.S. Pat. No. 3,769,398, which discloses non-ionic hair shampoo formulations containing an active ingredient such as a betaine, sulfo betaine, amine oxide or mixture thereof, a water soluble polymer such as a polyethyleneimine-ethylene oxide or propylene oxide polymer or a propoxylated polyethyleneimine.
3. U.S. Pat. No. 4,329,335, which describes an amphoteric, nonionic anti-dandruff shampoo containing an active agent (1-imidazalyl-1-) (chlorophenoxy-3,3-dimethylbutane-2-one) and amphoteric surfactants. DMAAC is disclosed as a preferred quaternized ammonium compound in this patent.
4. Published European Patent Application No. 74,819, which discloses an anti-dandruff cream rinse conditioner containing zinc pyrithione, glucan or guar gum, hydroxyethyl cellulose and a homopolymer of DMAAC or a copolymer of DMAAC and acrylamide.
5. U.S. Pat. No. 3,996,146, which discloses a shampoo formulation comprising from 0.05 to about 2.5%, by weight, of a cationic resin including quaternary polymers derived from dimethyl diallyl ammonium salts.
6. U.S. Pat. No. 4,040,984, which discloses polymers useful for preparing electroconductive paper which comprise quaternary diallyl dialkyl ammonium monomers and acrylic acid.
7. U.S. Pat. No. 3,912,808, which discloses a composition and method for waving or straightening hair using an aqueous solution of a reducing agent and a water soluble secondary or tertiary amine polymer or a polymer of diallyl amine or a quaternary polymer of diallyl dialkyl ammonium salts. This patent also discloses the use of dialkyl ammonium polymers which contain acrylamide or diacetone acrylamide. The use of dimethyl diallyl ammonium chloride/acrylic acid polymers is not disclosed or suggested.
8. U.S. Pat. No. 4,027,008, which discloses hair treating compositions which contain a water-soluble secondary or tertiary amine polymer or a polymer of diallyl amine or a quaternary polymer of diallyl dialkyl ammonium salts.
9. U.S. Pat. No. 3,986,825, which discloses the use of dialkyl diallyl ammonium polymers in cosmetic products, including copolymers of a dialkyl diallyl ammonium monomer and acrylamide or diacetone acrylamide.
10. U.S. Pat. No. 4,764,365, which discloses the use of DMAAC/acrylic acid polymers such as Merquat 280 to improve the feel of personal care products. This patent discloses that commonly used antiperspirants include aluminum zirconium complex, aluminum chlorohydrate and the like. However, this patent does not disclose or suggest that DMAAC/acrylic acid-type polymers may be used to thicken metal-containing aqueous solutions generally or aluminum-containing personal care products.
11. U.S. Pat. No. 4,772,462, which discloses the use of DMAAC/acrylic acid-type polymers in shampoos, conditioners, rinses, bleaches, hair dyes and hair sprays.
12. U.S. Pat. No. 4,675,178, which relates to stable deodorant compositions which contain DMAAC polymers and aluminum antiperspirant agents.
13. Copending application U.S.S.N. 794,981 discloses the use of DMAAC/acrylic acid-type polymers in deodorant formulations.

In summary, though the use of dialkyl diallyl ammonium chloride-type polymers, including DMAAC-acrylic acid type polymers, in personal care products is known, the use of polymers containing a diallyl dialkyl ammonium monomer and acrylic acid for the purpose of thickening aqueous solutions or personal care product compositions is not known or suggested in the art. These polymers are particularly effective when used to provide thickening to liquid personal care products, such as roll-on deodorant/antiperspirants, and generally do so without imparting color to water-white formulations.

DETAILED DESCRIPTION OF THE INVENTION

The instant invention is directed to a method for thickening metal-containing aqueous compositions or solutions, such as liquid, water-based, metal-containing personal care product compositions or intermediates, comprising adding to such a composition or solution an effective amount of a polymer comprising:

a) about 1 to about 99%, based on total polymer weight, of a quaternary diallyl dialkyl ammonium monomer, wherein alkyl groups are independently selected from alkyl groups of 1 to 18 carbon atoms, preferably C₁₋₄ alkyl, and wherein said quaternary diallyl dialkyl ammonium monomer's counterion is selected from the group consisting of conjugate bases of acids having an ionization constant greater than 10⁻¹³, more preferably, selected from the group consisting of fluoride, bromide, chloride, hydroxide, nitrate, acetate, hydrogen, sulfate, and primary phosphates; and

b) about 1 to about 99%, based on total polymer weight, of an anionic monomer selected from the group consisting of acrylic acid and methacrylic acid; wherein the weight average molecular weight of said polymer ranges from about 5,000 to about 6,000,000, as determined by gel permeation chromatography.

The instant invention is also directed to thickened metal-containing aqueous compositions or solutions, such as thickened, personal care product compositions, which contain the above described polymer.

As used herein, the phrase "personal care product composition or solution" includes, but is not limited to, metal-containing hand and face lotions, soaps and creams, suntan lotions, bubble baths, shaving creams, antiperspirant and deodorant compositions or solutions.

As used herein, the term "metal-containing" refers to any aqueous composition or solution or personal care product formulation or product intermediate which contains a metal having a positive valence of greater than 2. Examples of metal ions of such metals include, but are not limited to, Al⁺³, Fe⁺³, Cr⁺³ and Ce⁺⁴. The most preferred metal is aluminum.

The most important class of aluminum-containing compositions are liquid personal skin care products, particularly roll-on antiperspirants. Such compositions are thickened by the instant polymers, as measured by the viscosity of the treated composition.

Personal skin care products generally comprise an active agent, such as a detergent, surfactant, conditioner, emollient, antimicrobial, antiperspirant and/or moisturizing agent. These products may also contain aluminum in the form of aluminum stearate, aluminum acetate, aluminum sulfate or other aluminum salt. Also, the active agents themselves may contain aluminum. For example, commonly used antiperspirants include, but are not limited to, aluminum zirconium complex, aluminum chlorohydrate and the like. For this reason, a preferred use of the instant polymer is for thickening water-based, liquid antiperspirant compositions, such as roll-on antiperspirants/deodorants. In the past, such compositions were generally thickened by the addition of emulsifying or dispersing fatty compounds, such as glycol stearates, cetyl alcohol or stearyl alcohol.

In its broadest sense, an effective amount of at least one of the instant polymers may be added to an aqueous solution, such as a liquid personal care product composition, in conjunction with a metal, such as aluminum, to thicken the solution being treated, if the solution does not contain a metal and the addition of a metal and at least one of the instant polymers does not cause compatibility or other problems.

As used herein, the term "effective amount" refers to that amount of polymer required to provide the desired thickness to the aqueous solution or aqueous-based product being treated. Generally, for compositions which contain a metal, the instant polymers are added at a dosage of greater than or equal to about 0.01% active polymer solids, based on the total weight of the liquid composition being treated. As the polymer dosage increases, assuming the presence of a suitable metal, the composition thickness as measured by viscosity generally increases from a water-like consistency to the consistency of a gel. Preferably, the dosage is about 0.01% to about 30% active polymer solids, based on the total weight of the metal-containing product to which the polymer is added. Most preferably, the polymer dosage should range from about 0.5% to about 12% active polymer, based on the total weight of the composition being thickened.

In the case where the aqueous solution or liquid personal care product to be thickened does not contain a metal having a positive valence of greater than 2, about 1.0 to about 50.0% of a suitable positive valence metal ion source, based on the total weight of the product being treated, can be added for the purpose. Any source of metal ions which is compatible with the solution, composition, intermediate or product to be thickened can be used. The amount of multivalent metal ions to be added varies depending upon the desired degree of thickening, the concentration of competing ions, if present, the anionic content of the polymer to be used and the specific metal ion added. In general, for a given polymer concentration, viscosity will increase with increasing metal ion concentration until the molar ratio of the metal ions to the total anionic functionality of the polymer (for example, the carboxylic functionality of an acrylic acid-based polymer), exceeds about one. Although the use of excess metal ions above this ratio is not harmful, it is not believed to cause a further thickening of a

system being treated.

Further, ion solubility generally depends upon the pH of the aqueous system being treated. Also, the presence of other metal chelating or complexing anions, for example EDTA or NTA, can alter the ratio of metal ion to polymer necessary to obtain a designated thickness. The effective amount of metal ion is further influenced by the application pH, because the ratio of protonated to free carboxylate groups for a carboxylic group-containing polymer is a function of pH. The exact nature of this interaction depends on the disassociation constant of the carboxylic functional group, which varies with structure. For these reasons, the optimal metal ion to polymer ratio should be determined experimentally for each specific application. Notwithstanding the above considerations, the upper concentration of the metal ion source is oftentimes determined based on solubility considerations.

In addition to the metal ion source, an effective amount of at least one of the instant polymers is added, based on the desired thickness and the amount of metal ion source added. The instant polymers, and a metal ion source, if needed, can be added to aqueous solutions or compositions such as personal care product compositions by any convenient method. Order-of-addition is generally not critical. Mixing may be utilized to quickly disperse the polymer into the composition being treated.

The quaternary diallyl dialkyl ammonium monomer may comprise from about 1 to about 99%, based on total polymer weight, of the polymer while the anionic monomer may comprise from about 1 to about 99%, based on total polymer weight. Preferably, the quaternary: anionic weight ratio is from about 95:5 to about 50:50, and most preferably from about 95:5 to about 65:35, based on the total weight of polymer. Thus, in the polymers of the present invention, the cationic moiety of the polymer is preferably predominant while the anionic moiety of the polymer is preferably minor. Additionally, other moieties may be present in the instant polymers; for example, acrylamide or other nonionic moieties may be present.

An especially preferred polymer is that where the cationic portion is dimethyldiallyl ammonium chloride (DMAAC) or diethyldiallyl ammonium chloride (DEDAAC) and where anionic portion is acrylic acid. Preferably, the DMAAC/DEDAAC:acrylic acid weight ratio ranges from about 95:5 to about 50:50, most preferably from about 95:5 to 65:35, based on total polymer weight.

The polymers of the instant invention may have any molecular weight ranging from about 5,000 to about 6,000,000, with the preferred molecular weight ranging from about 100,000 to about 5,000,000. The most preferred viscosity for the instant polymers ranges from about 4,000 to about 10,000 cps, as determined using a Brookfield LVF No. 4 spindle at 60 rpm. These polymers may be prepared using any conventional free radical polymerization technique, such as the technique disclosed by Butler and Angelo, "Journal of American Chemical Society," Vol. 79, p. 3128 (1957) or the technique suggested in U.S. Reissue Patent No. 28,543.

The most preferred polymers of the instant invention are commercially available copolymers of dimethyldiallyl ammonium chloride and acrylic acid which are sold as Merquat 280 by Calgon Corporation. Merquat 280 contains 80/20 (w/w) dimethyldiallyl ammonium chloride/acrylic acid and has a molecular weight of approximately 1 million.

Exemplary of the best mode is the use of Merquat 280 to thicken a water-based antiperspirant composition. Such compositions typically contain water, a glycol such as propylene glycol and an aluminum-containing antiperspirant. Because of the water-like consistency of such compositions, they generally must be thickened so that they do not flow too rapidly or easily past the balls of roll-on dispensers. An effective amount of Merquat 280 is added so as to yield the desired thickness.

Thus, in the best mode, an effective amount of Merquat 280 is added to a liquid aluminum-containing antiperspirant formulation capable of being topically administered wherein said formulation comprises water, an effective aluminum-containing antiperspirant, a glycol such as propylene glycol and optionally a deodorant and/or one or more cosmetically acceptable excipients such as buffers, fragrances and/or preservatives. The polymer is added in an amount sufficient to increase thickness to the desired consistency. The actual amount of polymer to be added depends primarily upon the desired thickness and the amount of aluminum in the composition being thickened. Generally, the preferred amount of Merquat 280 added will range from about 0.01% to about 30% active polymer, based on the total weight of the composition being thickened. Most preferably, the Merquat 280 dosage will range from about 0.5 to about 12% active polymer.

Typically a thickened antiperspirant formulation may be achieved by mixing at least one of the instant polymers with de-ionized water, followed by addition of the other ingredients. For example, an emulsifier may be added with agitation followed, in some instances, by heating to a temperature ranging from 65° to 90°C (preferably 75° to 80°). Agitation is then typically continued while adding at least one antimicrobial agent, followed by the addition of preservatives, buffers, dyes, and/or fragrances, and an antiperspirant agent.

The amount of antiperspirant agent used varies over a wide range and depends on the specific agent employed. Generally, an effective amount for the purpose is used. Representative antiperspirants within the scope of the invention include, but are not limited to, aluminum zirconium complex, aluminum chlorohydrate,

aluminum chlorohydrate P.G. and the like.

Generally, the amount of polymer employed in the practice of the invention ranges from about 0.01% to about 30% polymer, by weight, based on the total weight of the formulation being treated. The remaining portion of the total composition contains the antiperspirant agent, water and conventional acceptable excipients.

5 Representative antimicrobial agents employed in the antiperspirant compositions of this invention include, but are not limited to, (2,4,4'-trichloro carbanilide), triclosan (2,4,4'-trichloro-2'-hydroxy diphenyl ether), benzalkonium chloride, zinc phenosulfonate, zinc ricinoleate and the like.

10 Representative emollients, humectants and moisturizing agents useful in such compositions include, but are not limited to, C₁₂₋₁₅ alcohol benzoates, sorbitol, glycerin, propylene glycols (PEG), lanolin, vegetable oils, mineral oils, isopropyl myristate, aloe vera, jojoba oil and the like.

Other cosmetically acceptable excipients that such formulations may contain include, but are not limited to, buffering agents and preservatives. Suitable water soluble preservatives are sodium bisulfate, sodium thiosulfate, ascorbate, benzalkonium chloride, glydant chlorobutanol, thimerosal, phenylmercuric borate, parabens, Tektamer[®] 38(1,2-dibromo-2,4-dicyanobutane) (Tektamer is a registered trademark of Calgon Corporation, Pittsburgh, PA.), benzyl alcohol, phenylethanol and the like. Suitable water soluble buffering agents are 15 alkali or alkali earth carbonates, phosphates, bicarbonates, citrates, borates, acetates, acid anhydrides, succinates and the like, such as sodium phosphate, citrate, borate, acetate, bicarbonate and carbonate. These agents may be present in amounts sufficient to maintain some optimum pH of the system in the range 2 to 9. As such, the buffering agent can be as much as 20% on a weight basis of the total composition. Additional 20 active agents are fully described in U.S. Pat. No. 3,986,825.

Generally, the amount of polymer employed in the practice of the invention ranges from about 0.01% to about 30% polymer, by weight, based on the total weight of the formulation being treated. The remaining portion of the total composition contains the antiperspirant agent, water and conventional acceptable excipients.

25 Known deodorant/antiperspirant manufacturing processes may require heat to bring conventional thickeners such as Cab-o-sil into solution. Such processes may be difficult to control and oftentimes result in a translucent or opaque products. By contrast, the instant method of thickening may generally be carried out at room temperature, is easy to control and generally results in a clear, water-white product.

30 EXAMPLES

The following examples, which further demonstrate the instant invention, are not intended to limit the scope of this invention in any way.

35 Examples 1-2

These examples demonstrate the use of the instant polymers in two (2) antiperspirant personal care product formulations:

	<u>Example 1</u>	<u>Example 2</u>
40 Merquat 280	1.0 to 10.0	1.0 to 3.5
Water, D.I.	24 - 33	51.5 - 54
45 Propylene Glycol	16.0	16.0
Aluminum Chlorohydrate	50	-
Aluminum-		
50 Zirconium Chlorohydrate	-	29.0

Examples 3-6

55 These examples demonstrate the ability of the instant polymers to increase the thickness of water-based aluminum-containing antiperspirant compositions.

5		Example No.			
		<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
	Merquat 280 Weight %	-	3.5	-	2.0
	Deionized Water Weight %	34.0	30.5	30.0	28.0
10	Propylene Glycol Weight %	16.0	16.0	16.0	16.0
	D.C. ACH 303				
	Aluminum Chlorohydrate Weight %	50.0	50.0	-	-
15	D.C. AZG 368				
	Aluminum Zirconium				
	Chlorohydrate Glycine Weight %	-	-	54.0	54.0
20	Visc. (cps)	11.5	25.0	6.8	23.5

In these examples, viscosity was measured by a Brookfield Viscometer, Model LVT, spindle #2 at 30 rpm.

Claims

- 30 1. A method for thickening a metal-containing, aqueous composition comprising adding to said composition an effective amount of a polymer comprising:
 - a) about 1 to about 99%, by weight, based on the total weight of said polymer, of a quaternary diallyl dialkyl ammonium monomer, wherein alkyl groups are independently selected from alkyl groups of 1 to 18 carbon atoms and wherein said quaternary diallyl dialkyl ammonium monomer's counterion is selected from the group consisting of bases of acids having an ionization constant greater than 10^{-13} ,
 - 35 b) about 1 to about 99%, by weight, based on the total weight of said polymer, of an anionic monomer selected from the group consisting of acrylic acid and methacrylic acid; wherein the weight average molecular weight of said polymer ranges from about 5,000 to 6,000,000, as determined by gel permeation chromatography.
- 40 2. The method of Claim 1, wherein said alkyl group of a) is C_{1-4} .
3. The method of claim 1, wherein a) is selected from the group consisting of dimethyl diallyl ammonium chloride and diethyldiallyl ammonium chloride and b) is acrylic acid.
- 45 4. The method of claim 1, wherein said effective amount ranges from about 0.01 to about 20%, by weight, of said product.
5. The method of Claim 1, wherein said aqueous composition is a water-based personal care product which contains aluminum in the form of an aluminum stearate, aluminum acetate, aluminum sulfate, aluminum zirconium complex, aluminum chlorohydrate or aluminum chlorhydrex P.G.
- 50 6. The method of Claim 5, wherein said personal care product is a water-based antiperspirant and wherein said aluminum is in the form of aluminum zirconium complex, aluminum chlorohydrate or aluminum chlorhydrex P.G.
- 55 7. The method of Claim 1, wherein said counterion is selected from the group consisting of fluoride, chloride, bromide, hydroxide, nitrate, acetate, hydrogen sulfate and primary phosphates.

8. A thickened, water-based liquid antiperspirant which comprises:
 - a) 1 to 95% water, by weight;
 - b) 1 to 50% of aluminum-containing an antiperspirant, by weight; and
 - c) an effective amount for thickening purposes of a copolymer comprising:
 1. about 1 to 99%, by weight of said polymer, of a monomer selected from the group consisting of dimethyl diallyl ammonium chloride and diethyldiallyl ammonium chloride; and
 2. about 1 to about 90%, by weight of said polymer, a monomer selected from the group consisting of acrylic acid, and methacrylic acid; wherein said polymer has a weight average molecular weight ranging from about 5,000 to about 6,000,000, as determined by gel permeation chromatography.
9. The composition of Claim 9, wherein said aluminum-containing antiperspirant compound is selected from the group consisting of aluminum zirconium complex, aluminum chlorohydrate, and aluminum chlorohydrate P.G.
10. A method for thickening an aqueous solution comprising adding to said solution an effective amount of:
 - A) a polymer comprising:
 - a) about 1 to about 99%, by weight, based on the total weight of said polymer, of a quaternary diallyl dialkyl ammonium monomer, wherein alkyl groups are independently selected from alkyl groups of 1 to 18 carbon atoms and wherein said quaternary diallyl dialkyl ammonium monomer's counterion is selected from the group consisting of bases of acids having an ionization constant greater than 10^{-13} ,
 - b) about 1 to about 99%, by weight, based on the total weight of said polymer, of an anionic monomer selected from the group consisting of acrylic acid and methacrylic acid; wherein the weight average molecular weight of said polymer ranges from about 5,000 to 6,000,000, as determined by gel permeation chromatography.
 - B) a metal ion having a positive valence of greater than 2, wherein the molar ratio of said metal ion to the carboxylic functionality of said polymer is greater than 1.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 8792

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 5)
D,X	EP-A-0 266 111 (CALGON CORP.) * Whole document * & US-A-4 764 365 ---	1-10	A 61 K 7/32 A 61 K 7/48 A 61 K 7/06
D,A	EP-A-0 200 548 (CALGON CORP.) * Whole document * & US-A-4 675 178 ---	1-10	
D,A	EP-A-0 269 243 (CALGON CORP.) * Claims * & US-A-4 772 462 ---	1-3	
D,A	EP-A-0 074 819 (AMWAY CORP.) * Claim 15 * -----	1-4	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 5)
			A 61 K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17-12-1991	Examiner COUCKUYT P.J.R.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 (04/91) (P0401)

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 701 812 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
20.03.1996 Bulletin 1996/12

(51) Int Cl.⁶: **A61K 7/32**

(21) Application number: **95306345.0**

(22) Date of filing: **11.09.1995**

(84) Designated Contracting States:
DE ES FR GB IT

(30) Priority: **16.09.1994 US 307121**

(71) Applicant: **DOW CORNING CORPORATION**
Midland, Michigan 48686-0994 (US)

(72) Inventors:
• **Abrutyn, Eric Steven**
Midland, Michigan (US)

- **Froix, Michael**
Mountainview, California (US)
- **Disaplo, Alfred Joseph**
Greenwich, Connecticut (US)
- **Springer, Jeffery T.**
La Honda, California (US)

(74) Representative: **Vandamme, Luc Johan Roger**
Dow Corning Limited,
Cardiff Road
Barry, South Glamorgan CF63 2YL, Wales (GB)

(54) **Adsorption of sweat components with a macroporous copolymer**

(57) A method of preventing underarm malodor associated with human perspiration. There is applied to the skin of a human, a safe and effective amount of a macroporous crosslinked copolymer containing acrylate or methacrylate units. Components of sweat such as fatty acids found in human perspiration, are adsorbed and entrapped into and within the confines of the macroporous copolymer. The macroporous copolymer possesses a pore diameter of a size sufficiently small to inhibit skin

bacteria from entering. Decomposition of fatty acid and sweat components by the skin bacteria is thereby retarded, and hence the generation of body malodor is reduced. The macroporous copolymer may be applied to the human skin in the form of a deodorant stick, a deodorant cream, a deodorant lotion, a deodorant spray, a deodorant roll-on, a deodorant pad, a pressed powder deodorant, a loose powder deodorant or a deodorant gel.

EP 0 701 812 A1

Description

This invention is directed to the adsorption of fatty acids and other components of sweat typically found in human perspiration. More particularly, it is directed to the adsorption and entrapment of sweat components within the confines of a macroporous copolymer. The macroporous copolymer must have a pore diameter sufficiently small to inhibit skin bacteria from entering.

Fatty acids such as propionic acid, butyric acid, and hexanoic acid, together with other components of sweat such as certain proteinaceous wastes, are among the primary components of axillary perspiration associated with body malodor. Upon reaching the surface of human skin, these materials are attacked by the bacterial flora which is pervasive on the skin. The materials are decomposed by the flora into volatile low molecular weight fatty acids such as isovaleric acid, caproic acid, and caprylic acid, in addition to certain mercaptans and aromatic amines, and hydrogen sulfide. These volatile products are the cause of body malodor.

Body malodor is most commonly combated with the aid of an underarm product such as a deodorant. Deodorants contain, among other ingredients, an antimicrobial agent which is intended to function in reducing the number of microorganisms found on the skin surface. Thus, the antimicrobial agent acts to reduce the bacterial flora present on the skin. In theory, this tends to reduce the decomposition which occurs on the skin, which in turn removes the cause of body malodor.

One of the most common antimicrobial agents employed as the active ingredient in underarm deodorant applications is TRICLOSAN. TRICLOSAN is the International Nomenclature Cosmetic Ingredient (INCI) name assigned by The Cosmetic, Toiletry and Fragrance Association (CTFA), Washington, D.C. for a substituted diphenyl ether compound, 5-chloro-2-(2,4-dichlorophenoxy) phenol or $C_{12}H_7Cl_3O_2$.

While TRICLOSAN is effective in its function in underarm deodorant applications, it as well as other commonly used antimicrobial agents are potentially "bad actors", in contributing to minor skin irritations in certain sensitive individuals. Therefore, a reduction in the amount of antimicrobial agent necessary for any given underarm application, would offer a distinct advantage in the marketplace, since a perceivable increase in mildness and a lower potential for skin irritation could result.

We have unexpectedly found that certain adsorbent copolymers exhibit effective sequestering of at least three fatty acids typically found in perspiration. While these copolymers are capable of entrapping the fatty acids and other sweat components because of their macroporous structure, they nevertheless possess a small enough pore diameter to inhibit entry of bacteria. By adsorbing fatty acids into the macroporous copolymer, these fatty acids are effectively isolated from decomposition by the bacterial flora found on skin, and the generation of body malodor is thereby significantly reduced.

Thus, the problem solved by the present invention involves the removal and isolation of fatty acids and other sweat components responsible for body malodor from skin flora to reduce the generation of body odor. According to the invention, this problem is solved by selectively adsorbing and entrapping the fatty acids and other sweat components within the confines of a highly crosslinked macroporous copolymer.

Thus, our invention introduces a method of preventing underarm malodor associated with human perspiration. According to the invention, there is applied to the skin of a human, a safe and effective amount of a macroporous crosslinked copolymer. Components of sweat, in particular fatty acids found in human perspiration, are surprisingly adsorbed and entrapped within the confines of said copolymer. The macroporous copolymer possesses a pore diameter of a size sufficiently small to inhibit skin bacteria from entering. Decomposition of these fatty acids by the skin bacteria is thereby retarded, and hence the generation of body malodor is reduced.

Preferably, the macroporous copolymer has pores with a distribution of pore diameters of between 0.0001 to 0.1 micrometer. The macroporous copolymer is in the form of particles having a particle size of between 1 to 80 micrometers in diameter. The macroporous copolymer may be applied to the skin as an ingredient of a formulated underarm product such as a deodorant stick, a deodorant cream, a deodorant lotion, a deodorant spray, a deodorant roll-on, a deodorant pad, a deodorant pressed powder, a deodorant loose powder or a deodorant gel.

Adsorbent macroporous copolymers are described in U.S. Patent 4690825, US Patent 4724240 and in a published European Patent Application 0 369 741 A2. Such materials are sold under the trademarks MICROSPONGE® by Advanced Polymer Systems Inc., Redwood City, California, and as POLYTRAP® by Dow Corning Corporation Midland, Michigan.

Evaluations of these adsorbent copolymers have demonstrated their effective sequestration of perspiration fatty acids such as propionic acid, butyric acid, and hexanoic acid, from solutions of these acids which approximate normal concentrations of human perspiration. These adsorbent copolymers inhibit the ingress of skin bacteria but allow the ingress of the fatty acids. In underarm applications, these adsorbent copolymers exhibit positive sensory characteristics.

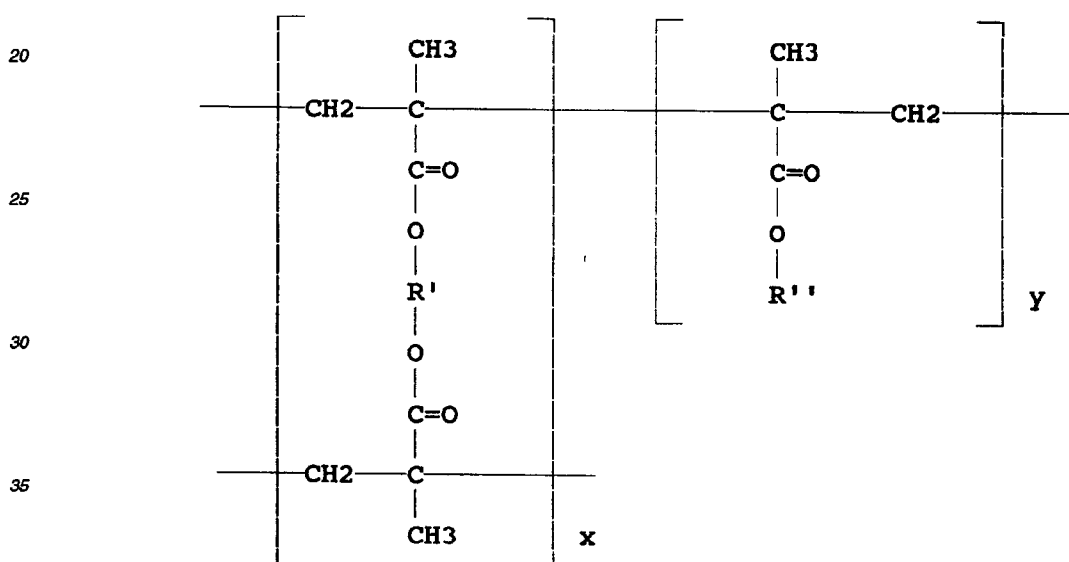
By including such copolymers as an ingredient of a deodorant product, it is possible to minimize or prevent the bacterial decomposition of perspiration components responsible for body malodor. Simultaneously, the deodorant products are imbued with improved sensory aesthetics. These copolymers have not been found to be incompatible with other deodorant ingredients such as fragrances and substantivity aids, regardless of form delivered to the skin.

The perspiration fatty acids are preferably "entrapped" within particles of a macroporous highly crosslinked copolymer containing acrylate or methacrylate units. These particles are not water soluble. Such macroporous materials are preferably manufactured in the form of spherical beads. Other forms of the adsorbent material can be employed such as a complex POLYTRAP® particulate which consists of a mixture of unit particles, agglomerates and aggregates.

These hydrophobic copolymeric materials are used to entrap the fatty acids and other components of sweat and are highly macroporous. Thus, the materials possess an inordinate amount of interstitial space including a vast labyrinth of voids. The material is capable of adsorbing several times its own weight of sweat components including fatty acids. Since the process involved is adsorption in contrast to absorption, the properties of both the copolymeric material and the entrapped sweat components are not altered.

The fatty acids are entrapped within the material in contrast to being encapsulated. Encapsulation connotes a complete enclosing of one material within another such as a shell formed around a core of liquid. Encapsulated ingredients are released by mechanical disruption of the shell or dissolution of the shell. Once the shell is disrupted, the entire contents of the shell are released or extracted. In entrapment, however, the release of an entrapped component is controlled or sustained by wicking, evaporation or capillary action. Mechanical disruption is not required.

The discrete particles of the hydrophobic macroporous materials of the present invention are free flowing particulates, even when loaded with an entrapped component. One copolymer representative of one species of a genus of these materials has the formula:



In this species of copolymer, x and y are integers in which the ratio of x:y is from 1:99 to 99:1. R' is the alkylene radical $(-\text{CH}_2\text{CH}_2)_a$, in which a is an integer having a value of from one to eight. R'' is the alkyl group $(-\text{CH}_2)_b\text{CH}_3$ in which b has a value of from zero to twenty-nine. In a more limited form of this particular species, the ratio of x to y is about 80:20. R' is $-\text{CH}_2\text{CH}_2-$ and R'' is $-\text{CH}_3$ or $(-\text{CH}_2)_{11}\text{CH}_3$, although the genus of these copolymeric materials is not so limited.

Suspension polymerization is one preferred technique which is used to produce these adsorbent macroporous materials. According to that particular technique, polymerization is carried out in water. The monomers, a volatile hydrocarbon solvent or material acting as a porogenic agent and a catalyst are combined and form beads or droplets in water and polymerization occurs within each bead. A surfactant or a stabilizer such as polyvinyl pyrrolidone is required to prevent the individually formed beads and droplets from coalescing in the solution. The resulting beads have a substantially spherical outer crust or shell, but reveal an interior macroporous structure.

The bead is typically 1 to 80 micrometers in average diameter. The particle diameter is controlled as a function of the rate of agitation used during the suspension polymerization process. The macroporous copolymer must have a pore diameter, in this application, of a size sufficiently small to inhibit skin bacteria from entering. Thus, a pore diameter of between 0.0001 to 0.1 micrometer is most preferred. The process for making the macroporous copolymer with such a controlled pore diameter is described in detail in US Patent 4690825. For example, according to that patent, the porosity is increased by increasing the crosslinking density or by increasing the concentration of the porogenic agent in the solution.

Other stabilizers and protective colloids such as starch, polyvinyl alcohol, carboxymethyl cellulose, methyl cellulose, or inorganic divalent alkali metal hydroxides such as MgOH, may also be used in place of polyvinyl pyrrolidone in this

suspension polymerization process. When the volatile hydrocarbon solvent or porogenic agent is removed, it leaves behind an empty porous copolymer bead.

Typically, two or more monomers are used in the process. One monomer is usually a polyunsaturated monomer and the other monomer is a monounsaturated monomer. Representative polyunsaturated monomers which are used are ethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate; 1,3 butyleneglycol dimethacrylate; 1,4 butanediol dimethacrylate; 1,6 hexanediol dimethacrylate, neopentyl glycol dimethacrylate, bisphenol A dimethacrylate; divinylbenzene and trivinylbenzene; divinyltoluene and trivinyltoluene; triallyl maleate, triallyl phosphate, diallyl maleate and diallyl itaconate.

The monounsaturated monomers which are used are preferably methacrylates and acrylates having straight-chain, branched-chain, or closed rings, with 5 to 30 carbon atoms, and more particularly those containing 5 to 18 carbon atoms. Representative of such preferred monounsaturated monomers are methyl methacrylate, lauryl methacrylate, 2-ethylhexyl methacrylate, methylhexyl methacrylate, isodecyl methacrylate, stearyl methacrylate, cyclohexyl methacrylate, and dimethylamino ethyl methacrylate. Other types of monounsaturated monomers such as styrene can also be used, however.

Highly crosslinked copolymeric systems consisting of particles of submicrometer size can also be prepared from monomers having at least two polymerizable unsaturated bonds and with no comonomers having a monounsaturated moiety. The details of the processes for making these adsorbent copolymers are found in any one of three patents, namely US Patent 4690825, US Patent 4724240 or the published European Patent Application 0 369 741 A2.

Standard texts generally define a fatty acid as a carboxylic acid derived from, or contained in an animal or vegetable fat or oil, and composed of a chain of alkyl groups of from 4 to 22 carbon atoms characterized by a terminal carboxyl group -COOH. However, for purposes of this invention, a "fatty acid" is also intended to include acids such as acetic acid and propionic acid.

The invention is illustrated in more detail in the following example. In the example, three of the known aliphatic carboxylic acid components of human sweat are used to study the sequestering power of macroporous copolymers sold under the trademark MICROSPONGE®. All of the macroporous MICROSPONGE® copolymers tested exhibited the ability to immobilize the three components of sweat. The three acids were propionic acid, butyric acid and hexanoic acid. These acids, however, were not equally sequestered by the macroporous copolymer adsorbent. It was found that the higher molecular weight aliphatic acid was retained the most.

Propionic acid, butyric acid, and hexanoic acid, were dissolved in water. A gas chromatographic assay was utilized with the aid of a polar NUKOL™ megabore Supelco™ column in a Hewlett-Packard™ 5890 chromatograph with split injection. Standard curves of the three acids were generated. To test each sample for sequestration, 100 milligrams of MICROSPONGE® macroporous copolymer was mixed with 10 milliliters of 500 parts per million of sweat acid. The MICROSPONGE® employed in these tests had a pore diameter which was between 0.0001 to 0.1 micrometer and a particle diameter which was between 1 to 80 micrometers. The solution was agitated on a rotating table for one hour, filtered through a 0.45 micrometer filter, and then injected into the gas chromatograph. The retention times for the three acids were 1.8 minutes for propionic acid, 2.4 minutes for butyric acid, and 4.2 minutes for hexanoic acid. The filtrate was analyzed after removal of the MICROSPONGE® macroporous copolymer. The concentration of the starting solution was 546 parts per million for propionic acid, 573 parts per million for butyric acid, and 533 parts per million for hexanoic acid. It was found that the acid remaining in the filtrate was about 75 percent for propionic acid, about 75 percent for butyric acid, and about 25 percent for hexanoic acid. Correspondingly, the amount of acid sequestered by the macroporous copolymer was about 25 percent for propionic acid, about 25 percent for butyric acid and about 75 percent for hexanoic acid.

The macroporous copolymer can be applied to the human skin in the form of a deodorant stick, a deodorant cream, a deodorant lotion, a deodorant spray, a deodorant roll-on, a deodorant pad, a deodorant pressed powder, a deodorant loose powder or a deodorant gel. Formulations for delivery of the macroporous copolymer in such deodorant applications are known in the art.

Thus, for delivery of the macroporous copolymer as a deodorant aerosol, there is combined with the macroporous copolymer, a propellant such as butane, isobutane, propane, isopropane, nitrogen, or carbon dioxide; a suspending agent such as an organofunctional clay, ethanol, or propylene carbonate; an aesthetic enhancer such as CYCLOMETHICONE, DIMETHICONE, isopropyl myristate, isopropyl palmitate, or a C₁₂ to C₁₅ alcohol benzoate; and a sensory additive such as a fragrance or talc.

For delivery of the macroporous copolymer as a deodorant roll-on, there is combined with the macroporous copolymer, an aesthetic enhancer such as CYCLOMETHICONE, an organic ester, or dioctyl adipate; a sensory additive such as a fragrance, talc, silica, or polyethylene; a solubilizer such as water or an alcohol; a viscosity builder such as silica, aluminum starch, or octenyl succinate; and an emulsifier such as glycerol monostearate, STEARETH 2, an alkoxyolate, or an organofunctional clay.

For delivery of the macroporous copolymer as a deodorant solid such as a stick, there is combined with the macroporous copolymer, a solidifier such as sodium stearate, cetyl alcohol, or stearyl alcohol; an aesthetic enhancer such

glycerin, propylene glycol, CYCLOMETHICONE, a C₁₂ to C₁₅ alcohol benzoate, an organic ester or an organic ether; and a sensory additive such as an emulsifier, a fragrance, talc, silica or polyethylene.

Other deodorant forms known in the art which are suitable for delivery of the macroporous copolymer are creams, pads, lotions, gels or powders. These other forms contain similar ingredients as those noted above. When added to a deodorant product, the product should contain 0.5 to 5 percent by weight of the macroporous copolymer. Amounts in excess of five percent can also be employed, to attain adequate adsorption of the fatty acids and other of the sweat components if necessary.

The hydrophobic macroporous copolymer is utilized in combination with a volatile component such as CYCLOMETHICONE, a fragrance, or ethanol, which is first incorporated into the copolymer and then into a deodorant product. Upon application to the axilla, the volatile component is volatilized, leaving the macroporous copolymer free to adsorb and entrap the components of sweat into and within confines of the copolymer.

Claims

1. A method of preventing underarm malodor associated with human perspiration comprising applying to the skin of a human, a safe and effective amount of a macroporous crosslinked copolymer containing acrylate or methacrylate units; sequestering and isolating the components of sweat found in human perspiration from decomposition by skin bacteria by adsorbing and entrapping the components of sweat found in human perspiration within the confines of the macroporous copolymer; the macroporous copolymer having a pore diameter of a size sufficiently small so as to inhibit skin bacteria from entering; whereby the components of sweat found in human perspiration are removed and isolated from decomposition by the skin bacteria and the generation of body malodor is reduced.
2. A method according to claim 1 in which the sweat components are fatty acids selected from the group consisting of butyric acid, propionic acid and hexanoic acid.
3. A method according to claim 1 in which the macroporous copolymer has a pore diameter of between 0.0001 to 0.1 micrometer.
4. A method according to claim 3 in which the macroporous copolymer is in the form of particles having a particle size of between 1 to 80 micrometers in diameter.
5. A method according to claim 2 in which there is adsorbed and entrapped within the confines of the macroporous copolymer an amount of from 25 to 75 percent by weight of the fatty acids.
6. A method according to claim 1 in which the macroporous copolymer is applied to the skin in a form selected from the group consisting of a deodorant stick, a deodorant cream, a deodorant lotion, a deodorant spray, a deodorant roll-on, a deodorant pad, a deodorant pressed powder, a deodorant loose powder and a deodorant gel.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 95306345.0
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 6)
A	EP - A - 0 570 085 (COLGATE-PALMOLIVE) * Claims 1,8 *	1,6	A 61 K 7/32
A	US - A - 5 281 413 (ERIC S. ABRUTYN et al.) * Claims 1-3,7,9 *	1,4,6	
D,A	EP - A - 0 369 741 (ADVANCED POLYMER SYSTEMS) * Claims 1,5 *	1,4	
A	US - A - 4 822 596 (MARTIN CALLINGHAM et al.) * Claims 1,2,5,6,12-15,17,18 *	1,4-6	
A	AT - B - 63 058 (UNILEVER) * Claim 1 *	1	
A	US - A - 4 650 670 (MARTIN CALLINGHAM et al.) * Claims 1,12 *	1,6	TECHNICAL FIELDS SEARCHED (Int. Cl. 6)
D,A	US - A - 4 724 240 (ERIC S. ABRUTYN) * Abstract *	1	A 61 K 7/00
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 27-11-1995	Examiner REIF
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 01.92 (P0401)

PATENT SPECIFICATION

957,175

NO DRAWINGS.

957,175



Date of Application and filing Complete Specification :

May 20, 1960.

No. 17929/60.

Application made in France (No. 795,194) on May 21, 1959.

Complete Specification Published : May 6, 1964.

© Crown Copyright 1964.

Index at Acceptance :—A5 B (31, 34, 35).

International Classification :—A 61 k.

COMPLETE SPECIFICATION.

Cosmetics in Gel Form and a Process for their Manufacture.

I, ANDRE FROMONT, of 89 avenue de Neuilly, Neuilly Sur Seine, France, of French nationality, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known to make a cosmetic product by perfuming a solution of high alcohol content with one or more essential oils. With varying degrees of difficulty, according to the oils taken, a solution is obtained which is filtered after having been allowed to stand at a very low temperature, usually in the region of 0° C. A liquid eau de Cologne is finally obtained. Known eaux de Cologne usually have a high alcohol content, 70° proof spirit being considered as a relatively weak concentration.

Use of liquid eau de Cologne has some drawbacks, however. It is not easy to judge the exact amount which it is desired to use, this fact bringing about loss upon the glove or the pad used to apply it. Carrying the eau de Cologne around in bottles is heavy and a nuisance. Its high alcohol content may lead to irritation or at least to considerably drying-up of the skin and accordingly produce disagreeable allergies.

To overcome these drawbacks, the present invention relates to a cosmetic which is brought to the state of a gel.

The invention consists in a process for the preparation of a cosmetic in gel form characterised in that small quantities of a highly polymeric carboxy-vinyl synthetic resin as herein defined and a dilute aqueous alcoholic solution of a weakly alkaline base are added to a liquid cosmetic.

As used herein, the term "highly polymeric carboxy-vinyl synthetic resin" is intended to refer to a polymer of acrylic or maleic acid, containing free —COOH groups.

It is to be understood that throughout the

Specification and claims the term "cosmetic" covers a wide range of products ranging from, e.g. perfumes to astringent and cleaning liquids. Moreover, throughout the Specification and claims a distinction is made between liquid cosmetics and cosmetics in gel form, and it is these latter, and more especially gelled perfumes, which are the object of the invention.

If the cosmetic is in gel form, it is more easy to get it out of its container (which may then be a pot or tube) in the correct quantity for the use desired. Similarly it is possible to apply the cosmetic to just that part of the body wished for without spilling as usually happens with a liquid cosmetic.

The liquid cosmetic may be prepared by known methods and then converted into a gel. Thus any alteration of known methods of preparing the cosmetic itself it avoided which makes the practical application of the present invention much simpler.

In a preferred mode of putting the invention into practice, the invention consists in a process for the preparation of a perfume in gel form characterised by dispersing a perfume in aqueous alcohol containing a surface-active agent, introducing with stirring a powdered highly polymeric carboxy-vinyl synthetic resin, allowing the resin to swell and introducing progressively a dilute aqueous alcoholic solution of weakly alkaline base to form the gel in the liquid perfume to give a perfumed jelly.

Gels thus obtained are stable, inert and accordingly easy to store. They are also easy to prepare cheaply and quickly. They are usually transparent. The cost and the alcohol content are both decreased compared with known preparations.

In a further preferred form, the invention still further consists in a perfume in gel form as described above in which less than 1% by weight of the composition of either

the synthetic resin or weakly alkaline base are used which eliminates any greasy or sticky feeling from the final product.

The surface-active agent referred to above lowers the surface tension of the liquid cosmetic. By reducing this surface tension it makes it easier for the ingredients to be wetted with the water.

The carboxy-vinyl resin which is then introduced into this solution containing the surface-active agent is wetted and swells. Some time is necessary for this swelling to be completed.

Then, by adding the alkaline base, the gel is formed in the cosmetic, giving a perfumed jelly, the pH and alcohol content of which may have been chosen within wider limits than hitherto possible for liquid cosmetics alone.

Gel formation may be made easier by warming the cosmetic, the resin and the alkaline base, or any other products going to make up the gel. Of course, the whole process may be carried out in the cold if the cosmetic is one which is damaged on heating.

It is particularly advantageous, according to another characteristic of the present invention to adjust the proportions of the various ingredients which make up the final gel in order to give a perfectly neutral product, i.e. a product of pH 7, thus avoiding any irritant effect upon the skin. If necessary, a pH slightly less than 7 may be chosen for those skins to which a slightly acid product is more suitable.

The invention may be further described with reference to the following non-limitative examples.

EXAMPLE 1.

Eau de Cologne in 70° proof spirit

Composition:—

Eau de Cologne, 70° proof ...	98—99%
Carboxy-vinyl synthetic resin ...	0.2—1.0%
Dilute aqueous alcoholic solution of weak alkaline base ...	0.2—1.0%
Total	100%

Procedure:—

Take the Eau de Cologne previously prepared in the liquid state, i.e. chilled and filtered in the region of 0°—5° C.

Put this Eau de Cologne in a vessel fitted with a good stirrer.

Start the stirrer at high speed and add the powdered carboxy-vinyl synthetic resin slowly to avoid formation of lumps.

Stir for about twenty minutes, allow to stand for the resin to swell for the requisite length of time, (which may be up to 12 hours).

Start the stirrer again and add very slowly the weak solution of alkaline base which has already been diluted with a portion of the water set aside for this purpose.

This addition immediately gives rise to gel formation and completes the preparation.

The product may be pumped for filling up the vessels it is to be contained in, and may be packed into tubes of various sizes, in jars with large mouths or in devices with perforated stoppers etc.

EXAMPLE 2.

Rose-perfumed eau de Cologne in 70° proof spirit.

Composition:—

	Weight Percentages	
Phenyl ethyl alcohol... ..	0.73	
Palmarosa, geranium essence	1.60	
1-citronellol	1.95	
Linalol	0.80	
Amber (in fragments) ...	0.20	
Essence de bois de Gaïac	0.20	
De-terpened geranium essence	3.00	
Benzyl acetate	1.00	
Rose essence (absolute) ...	0.50	
C ₁₂ aldehydes	0.01	
Citral	0.01	
96° proof alcohol	about 60—63	
Distilled water	about 25—27	
Carboxy-vinyl synthetic resin	0.2—1.0	
Dilute aqueous alcoholic solution of weak alkaline base	0.2—1.0	
Total	100	

Procedure:—

Prepare the eau de Cologne, by methods known *per se*, as a liquid i.e. mix the ingredients, chill and filter in the temperature range 0°—5° C.

Put this eau de Cologne in a vessel fitted with a good stirrer.

Start the stirrer at high speed and add the synthetic resin slowly to avoid formation of lumps.

Stir for twenty minutes, allow to stand for the swelling of the resin for the necessary length of time (which may be up to 12 hours).

Start the stirrer again and add the alkaline solution, which has been previously diluted with a portion of the water set aside for this purpose, very slowly.

The gel forms immediately after this addition and completes the preparation.

The gel may be then conditioned or stored.

EXAMPLE 3.

EAU DE COLOGNE IN AT LEAST 50° SPIRIT

Composition:—		By Weight
5	A { Concentrated Cologne essence	1.0—10%
	{ Polyoxyethylenated sorbitan monolaurate	1.0—10%
	B { 96° proof alcohol	20—50%
	{ Distilled water	20—50%
	C Carboxy-vinyl synthetic resin	0.2—10%
10	D Dilute aqueous alcoholic solution of weak alkaline base	0.2—10%
Total		100%

Procedure:—

Weigh the concentrated essential oils and the surface-active agents together and heat on a water bath to a sufficient temperature to solubilise the oils; allow to cool to room temperature after shaking to mix the constituents (A).

Dilute the concentrate A by adding the alcoholic solution B with moderate shaking.

Filter in the normal fashion without chilling, merely to hold back any gross impurities.

Put the solution obtained in a vessel fitted with a good stirrer.

Start the stirrer at high speed, and add the synthetic resin slowly to avoid formation of lumps.

Stir for about twenty minutes; allow to stand the necessary time for swelling of the resin (up to 12 hours may be necessary).

Start the stirrer again and then add the weak alkaline base solution, diluted with a portion of the water saved for this purpose, very slowly.

The gel forms instantly, completing the preparation. It may then be either immediately conditioned, or stored.

EXAMPLE 4.

REJUVENATING ANTI-WRINKLE JELLY.

Composition:—		Percentages by weight		
	A { Polyoxyethylenated sorbitan monopalmitate Concentrated perfume	0.2—10 0.05—0.5		
45	{ B { 90° proof alcohol Menthol C { Distilled water Allantoin	5—18 0.01—0.02 35—40 0.1—0.5		
50		{ D { Distilled water Witch-hazel Glycolisate of yeast Glycolisate of bramble Vitamin PP Diluted azulene	33—38 0—20 5—10 0.5—1.0 0.01—0.1 0.01—0.2	
55			F Carboxy-vinyl synthetic resin	0.2—1.0
			G Dilute aqueous alcoholic solution of weak alkaline base	0.2—1.0
	H Colouring agent		to 100	
Total			100%	

Procedure:—

5 Weigh together the surface active agent and the concentrated perfume; heat on a water-bath at a high enough temperature to solubilise the essential oils, stir to mix the constituents and allow to cool to room temperature (A).

Dissolve the menthol in the 96° proof alcohol separately (B).

10 Dissolve the allantoin in some of the distilled water (about 35% of the whole).

Warm to ensure complete solution. Allow to cool (C).

15 Mix B, C and D to obtain solution E and dilute solution A progressively with this solution, keeping the whole chilled and agitated.

Filter through an ordinary filter paper to remove gross impurities.

20 Put this filtered solution in a vessel fitted with a good stirrer.

Start the stirrer at high speed and add the synthetic resin slowly to avoid the formation of lumps.

25 Stir for twenty minutes, allow to stand for the time necessary for the swelling of the resin (up to twelve hours may be necessary).

Restart the stirrer and add slowly the weak alkaline solution, which has previously diluted with a portion of water saved for this purpose.

The gel forms instantly after this addition and completes the preparation. It may either by conditioned immediately or stored.

35 The jelly obtained is not sensitive to sudden changes in temperature, and has the unique property of liquefying completely during application, leaving the user greatly refreshed.

40 It gives the possibility of adding, to the maximum amount, all the desirable active agents without losing the consistency and without these active agents having their properties changed.

45 Not being prone to decay it can contain these constituents without it being necessary for other protection by antiseptics, which are more or less harmful to these preparations.

EXAMPLE 5.

COSMETIC FRUIT JELLY.

50

Composition:—

Weight Percentages

55	A	Concentrated natural fruit juice	1—50
		Synthetic fruit essence	1—5
		96° proof alcohol	0—20
		Distilled water	30—90
		Vitamin complex	0—10
		Antiseptic	0—0.5
60	B	Carboxy-vinyl synthetic resin	0.2—1.0
	C	Dilute aqueous alcoholic solution of weak alkaline base	0.2—1.0
	D	Colouring matter	to 100
Total			100%

Procedure:—

65 Weigh out and mix up A without warming and filter through a filter paper or through fine gauze.

Put A in a mixer fitted with a good stirrer.

70 Start this stirrer at high speed, and add synthetic resin B slowly to avoid the formation of lumps.

Stir for about twenty minutes and allow to stand for the necessary time for swelling (twelve hours may be needed).

75 Start the stirrer again and add slowly the alkaline solution (previously diluted with a portion of the water saved for that purpose).

The gel forms instantaneously after this

80 addition and completes the preparation. The product may be either conditioned immediately or stored.

The synthetic fruit essence may be replaced by a natural fruit essence.

85 By varying the active products in this jelly, substances may be obtained which have astringent, stimulating or soothing action.

Many different properties may be obtained starting from the same basic material, to clear up certain skin defects.

90 These special effects of its application are most interesting especially for a basically cosmetic product.

EXAMPLE 6.
AFTER-SHAVE LOTION.

Composition:—		Percentages by weight
5	A { Non ionic surface active agent Concentrated perfume	0.2—1.0 0.2—1.0
	D { B { 96° proof alcohol Crystallised menthol Hexachlorophene (G-11)	10—60 0.1—0.4 0.1—1.0
10	C { Distilled water Allantoin Witch-hazel	10—60 0.1—0.3 5—20
	E Carboxy-vinyl synthetic resin	0.2—1.0
15	F Dilute aqueous alcoholic solution of weak alkaline base	0.2—1.0 to 100
	G Colouring agent	to 100
Total		100%

Procedure:—

20 Warm the surface active agent and the perfume together on a water-bath to solubilise the essential oils, stir to mix and allow to cool to room temperature.

25 Dissolve the menthol and the G-11 in the 96° proof alcohol without heating to obtain B.

30 Dissolve the allantoin in a sufficient quantity of water by heating to the most convenient temperature on a water-bath, and allow to cool to obtain C.

Mix B and C to obtain D.

Dilute A progressively with D with moderate stirring.

35 Filter through ordinary filter paper without previous chilling to remove the gross impurities.

Put the solution obtained into a vessel fitted with a good stirrer.

40 Start the stirrer at high speed and add the synthetic resin slowly to avoid the formation of lumps.

Stir for about twenty minutes and allow to stand for the necessary length of time for the resin to swell (12 hours may be necessary).

45 Start the stirrer again and add very slowly the alkaline solution which has been diluted with a portion of the water saved for that purpose.

50 The gel forms instantaneously upon this addition, completing the preparation. It may then be either conditioned immediately or stored.

55 This new "after shave" gel has the indispensable properties of being antiseptic, astringent, soothing and cicatrizing. Moreover it has the advantage of being more easy to apply than a liquid contained in a bottle.

60 The new after-shave gel is very easy to use, the speed with which it spreads and dries, recommending itself particularly to men, who are not disposed to spend much time upon their toilette.

The gel leaves no sticky or fatty residue, unlike most existing products.

EXAMPLE 7.
HAIR DRESSING.

Composition:—		Percentages by weight
65	A { Polyoxyethylene stearate Convenient perfume	0.1—1.0 0.2—1.0
70	B { Distilled water 96° proof alcohol Antiseptic	30—98 0—70 0—0.5
	C Carboxy-vinyl synthetic resin	0.2—1.0
75	D Dilute aqueous alcoholic solution of weak alkaline base	0.2—1.0 to 100
	E Colouring agent	to 100
Total		100%

Procedure:—

5 Weigh up together the surface active agent and the perfume, warm upon a water-bath to a temperature high enough to solubilise the perfume, stir and allow to cool to room temperature (A).

Dilute concentrate A with solution B, under moderate stirring.

10 Filter upon an ordinary filter paper without chilling to remove the gross impurities. Put the solution obtained in a vessel fitted with a good stirrer.

15 Start the stirrer at high speed and add the synthetic resin slowly to avoid formation of lumps.

Stir for about twenty minutes and allow to stand for the necessary time for the resin to swell (12 hours may be necessary).

20 Start the stirrer again and very slowly add the alkaline solution diluted with a portion of the water saved for that purpose. The

gel forms instantly upon this addition, completing the preparation. It may be packed straight away, or stored.

25 The chemical gel obtained, differs from known hair dressings in that it leaves no residue and consequently does not clog up the hair.

30 Other known gels tended to putrify, and to generally decompose rather quickly and sometimes tend to liquify despite the presence of considerable quantities of antiseptic.

The new gel hair-dressing does not putrify, is not sensitive to temperature variations, and does not change in viscosity upon standing.

35 It can contain any active substance desired for hair treatment and has a brilliance which it gives to the hair, lubricating it while not greasing it.

40 It may be made up completely transparent if desired and is more attractive because of this than the other known hair dressings.

EXAMPLE 8.

DEODOURISING JELLY.

45	Composition:—	Percentages by weight
	A {Lauric alcohol-polyoxyethylene ether ...	0.5—5.0
	{Convenient concentrated perfume ...	0.5—5.0
50	D {	
	B {96° proof alcohol	20—50
	{Hexachlorophene	0.2—2.0
	C Distilled water	20—80
	E Carboxy-vinyl synthetic resin	0.2—1.0
	F Dilute aqueous alcoholic solution of weak alkaline base	0.2—1.0

55 Procedure:—

Weigh out together the surface active agent and the perfume, warm upon a water-bath to a high enough temperature to solubilise the essential oils, stir to mix and allow to cool to room temperature.

60 Dissolve the hexachlorophene in the 96° proof alcohol to give B and mix B and C together to obtain solution D.

65 Dilute concentrate A by adding solution D progressively with moderate stirring.

Filter through an ordinary filter paper, without chilling, merely to hold back the gross impurities. Put the filtrate into a vessel fitted with a stirrer.

70 Start the stirrer at high speed and add the synthetic resin slowly to avoid the formation of lumps.

75 Stir for about twenty minutes, and allow to stand at room temperature for the time necessary for the resin to swell (12 hours may be necessary).

Start the stirrer again and add very slowly the alkaline solution diluted with a portion of the water saved for this purpose.

80 The gel forms instantly after this addition

and completes the preparation. It may be conditioned straight away or stored.

The deodourising jelly obtained has the same advantages as the solid sticks already known.

85 It may contain alcohol to enhance evaporation.

It does not contain fatty or gluey substances which are disagreeable under the arms and spoil clothes.

90 It may be provided in distributors with perforated stoppers for direct application without the user having to handle the product.

It may equally well be provided in jars or tubes of any common type used for cosmetics.

100 Its preparation is very simple, necessitating as it does neither warming nor special equipment.

It is evident that the invention is not limited to the examples given above, but that many other variations may be made without departing from the scope of the invention.

In the above examples any weak alkaline base may be used, such as soda, ammonia,

alkaline carbonates or borates, hydroxyl-amides ethanalamines, propanolamines or ethylamines.

WHAT I CLAIM IS:—

- 5 1. A process for the preparation of a cosmetic in gel form characterised in that small quantities of a highly polymeric carboxy-vinyl synthetic resin as herein defined and a dilute aqueous alcoholic solution of a weakly alkaline base are added to a liquid cosmetic.
- 10 2. A process as claimed in Claim 1, in which less than 1% by weight of the composition of the carboxy-vinyl resin is used.
- 15 3. A process as claimed in Claim 2, in which less than 1% by weight of the composition of the alkaline base is used.
- 20 4. A process for the preparation of a perfume in gel form characterised by dispersing a perfume in aqueous alcohol containing a surface-active agent, introducing with stirring a powdered highly polymeric carboxy-vinyl synthetic resin as herein defined, allowing the resin to swell and introducing progressively a dilute aqueous alcoholic solution of weakly alkaline base to form the gel in the liquid perfume to give a perfumed jelly.
- 25 5. Process according to any one of the

Claims 1 to 4 characterised in that the liquid cosmetic mixture and products forming the gel are warmed to make the reaction easier and to give a more rapid gelling. 30

6. Process according to any one of the Claims 1 to 5 characterised in that the proportions of cosmetic, resin, and alkaline base are chosen so as to give a final product of pH7. 35

7. A process according to any one of Claims 4 or Claims 5 or 6 as dependent on Claim 4, modified in that the perfume is dispersed in water instead of aqueous alcohol. 40

8. A process as claimed in any one preceding claim in which further colouring materials and/or perfumes are added.

9. A process for producing a cosmetic in gel form substantially as hereinbefore described with reference to any one of the preceding examples. 45

10. A cosmetic in gel form prepared by the process substantially as described with reference to any one of the preceding examples. 50

MARKS & CLERK,
Chartered Patent Agents,
Agents for the Applicant.

